Note on the Boiling-point of Sulphur.

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As I have been partly to blame for the delay in the publication of the observations described in the preceding paper by Mr. N. Eumorfopoulos, it seems right that I should make a brief statement, by way of apology, with regard to the object of the work and the causes which have led to the delay.

The determination of the boiling-point of sulphur by Mr. E. H. Griffiths and myself in 1890* was made with the same air thermometer as that employed in my original experiments of 1887,† and gave the same value for the difference-coefficient of the platinum thermometer. The result depended, however, on the scale of the constant-pressure air thermometer, and the correction for the expansion of the bulb was deduced from observations of the linear expansion over the range 0° to 500° C. of a piece of glass tube from which the bulb was made. Some uncertainty was introduced also by changes in the volume of the bulb at a temperature of 450° C.

Shortly afterwards I succeeded in devising a much more delicate type of gas thermometer,‡ with compensated connecting tubes, and independent of barometric measurements, the bulb of which could be used as a mercury weight thermometer in determining the expansion correction. In the hope of obtaining a more accurate verification of the boiling-point of sulphur, as well as of the difference-formula for the platinum scale between 0° and 450° C., I undertook a series of observations in 1893 in conjunction with Mr. E. H. Griffiths and Mr. G. M. Clarke, employing two gas thermometers precisely similar to that described by Mr. Eumorfopoulos, except that they were made of English lead glass. One of these thermometers was filled with air and the other with hydrogen in the first instance. At a later stage both were filled with nitrogen, because it was found that hydrogen reduced the lead glass at high temperatures, and there was some reason to suspect action of oxygen on the mercury.

The English lead glass, when it had once been annealed in sulphur vapour, proved remarkably free from changes of volume, and there was no difficulty in determining its expansion in terms of mercury between 0° and 100° C., with

* 'Phil. Trans.,' A, 1891.
† 'Phil. Trans.,' A, 1887.
‡ 'Roy. Soc. Proc.,' vol. 50, p. 247.

an accuracy of the order of 1 or 2 milligrammes of mercury in 1300 grammes, corresponding to an error of about 1/2000 degree of temperature, but it was found that the results could not be brought into satisfactory agreement with Regnault's formula, or with the previous determination by the linear expansion method. Assuming Regnault's formula for the absolute expansion of mercury,

$$V/V_0 = 1 + 0{\cdot}00017901t + 0{\cdot}000{,}000{,}0252t^2,$$

the expansion of the lead glass bulbs could be approximately represented by the formula

$$V/V_0 = 1 + 0{\cdot}00002242t + 0{\cdot}000{,}000{,}0240t^2,$$

which may also be written (adopting the form employed by Eumorfopoulos)

$$V/V_0 = 1 + \{0{\cdot}00002482 + 0{\cdot}000{,}000{,}0240\,(t-100)\}\,t.$$

The expansion did not appear to follow accurately a parabolic law, but if a parabolic formula were assumed for mercury, the b term, or the coefficient of t^2, came out nearly the same as for mercury. The observations could be almost equally well represented by assuming the expansion of both mercury and glass to be uniform between 0° and 100° C., an assumption which also appeared to represent Regnault's observations on mercury over this range within the limits of experimental error. The effect of the b term on the temperatures deduced by gas thermometer is about 130 times as great at 445° C. as at 50° C., amounting, if $b = 24 \times 10^{-9}$, to 2°·64 at the S.B.P., and to 0°·020 at 50° C. Since the expansion did not appear to follow accurately a parabolic formula, it seemed useless to attempt an extrapolation. It appeared probable that the b term for mercury was not constant, as in Regnault's formula, but increased with rise of temperature; and that it would be necessary to make a redetermination of the absolute expansion of mercury, and also to employ the weight thermometer method at much higher temperatures than 100° C., if any certain result were to be obtained by this method. I accordingly designed a multiple manometer for the absolute expansion of mercury, in which the expansion to be measured was increased to about eight times that obtained by Regnault; and I hoped, by employing platinum thermometers and other refinements not available in his time, to be able to secure a much higher order of accuracy in this fundamental determination. At this point the work was interrupted by my appointment as Professor of Physics at McGill College, Montreal, in October, 1893, and I was unable to resume it until my return to University College in 1898.

Meanwhile the Kew Committee and the International Bureau of Sèvres, recognising the importance of the work, had collaborated in arranging a redetermination of the boiling-point of sulphur and of the scale of the

platinum thermometer, which was undertaken by Messrs. Chappuis and Harker.* The results of their work with a constant-volume nitrogen thermometer led to a somewhat higher value, namely 445°·26 C., of the S.B.P. than the value 444°·53 C. obtained with the constant-pressure air thermometer. The difference between these two values was too great to be explained by the difference between the scales of the constant-volume and constant-pressure thermometer, which probably amounts to only 0°·3 at this point.† But as I pointed out at the time,‡ the uncertainty of the expansion correction was sufficient to account for a much larger discrepancy. The results of Messrs. Chappuis and Harker depended on the extrapolation of a formula for the linear expansion obtained from observations over the range 0° to 80° C., which gave a comparatively high value for the coefficient b. They subsequently adopted a different formula for the expansion, which had the effect of reducing their result to 444°·77 C. on the constant-volume scale, which is in practically perfect agreement with 444°·53 on the constant-pressure scale.

Having regard to the excellence of this agreement it might have appeared superfluous to proceed further. But the uncertainty of inferring the cubical from the linear expansion still remained, and it was desirable to obtain a more accurate verification of the scale of the platinum thermometer at ordinary temperatures for the reduction of experiments on the variation of specific heat. My original gas thermometer had been broken on the way out to Canada, and again on the way back. I therefore had another constructed of Jena glass to fit the same stand, hoping that the new glass would prove less troublesome in respect of change of volume. At the same time I proceeded with the construction of the apparatus already designed for the absolute expansion of mercury. This was nearly finished, and several determinations of the S.B.P. had already been made by Mr. Eumorfopoulos, when I had to leave University College in April, 1902. After several fruitless efforts to find a place to set up the apparatus at the Royal College of Science, I had finally to await the completion of the new buildings, then in course of erection. I was able to proceed with the erection of the apparatus at the end of last year, and some preliminary experiments which promise well have already been made with it. The apparatus seems likely to realise the same order of accuracy in the absolute expansions of mercury as in the weight-thermometer tests of the bulb. It was designed with that intention, but, until it was set up and tested, it was difficult to foresee

* 'Phil. Trans.,' A. vol. 94, p. 74.

† 'Callendar, 'Phil. Mag.,' 1903, p. 93.

‡ 'Phil. Mag.,' December, 1899, p. 544.

whether effects of lag and viscosity might not be serious in so great a length of tubing.

It will be seen from the experimental results given by Mr. Eumorfopoulos in the preceding paper that the hopes which I had formed of Jena glass were far from realised. The continual changes of volume of the bulb were among the chief difficulties encountered, and are doubtless indirectly responsible for the apparent variations in the coefficient of expansion observed, which considerably exceed the limit of accuracy of reading. An alternative method of treating the observations, which I adopted in the experiments of 1890, would be to calculate the changes of volume by assuming a constant value of the coefficient. This would tend to eliminate the accumulation of accidental errors in a long series of weighings. In spite of the changes of the bulb, and of other possible sources of error, it is obvious that the results obtained by Mr. Eumorfopoulos are entitled to great weight, and will lead to a more certain value of the S.B.P. when the expansion of mercury has been more accurately determined. Publication has been delayed from time to time in the hope that these difficulties might be surmounted, but as it now appears certain that glass is an unsuitable material for accurate work of this nature, it would be useless to delay any longer. The description of the method and apparatus employed, which has not been previously published, although the apparatus has been in existence for so many years, may prove serviceable to others engaged in similar work.

That the final result given, namely, 443°·58 C. for the S.B.P., should be nearly 1° lower than the value previously admitted may appear surprising. But it must not be forgotten that, if Chappuis' formula for the expansion of mercury had been adopted, the result would have been 445°·8 C. approximately, or more than a degree higher than the old value. This illustrates the necessity for a redetermination of the expansion of mercury. At the same time it must be admitted that Regnault's formula is more likely to be right at the higher temperatures, and that the old value of the S.B.P. is likely to be too high in consequence of the probable error involved in deducing the cubical coefficient from the linear expansion of a tube.